Rapid Optical Detection of Organic Molecules and Water on Rock and Sediment Surfaces with Deep Ultraviolet Laser-induced Native Fluorescence

Pamela Conrad,[1] Arthur Lane,[1] Rohit Bhartia,[1] William Hug,[2] Michael Pelletier[1]
[1]Jet Propulsion Laboratory, California Institute of Technology
[2]Photon Systems Inc., Covina CA

JPL

We have developed an approach and an instrument for rapid detection of biological and organic chemicals on surfaces or in fluid volumes. By exciting organic molecules with a deep ultraviolet light source, we can quickly (in 50 microseconds) AND NON-INVASIVELY:

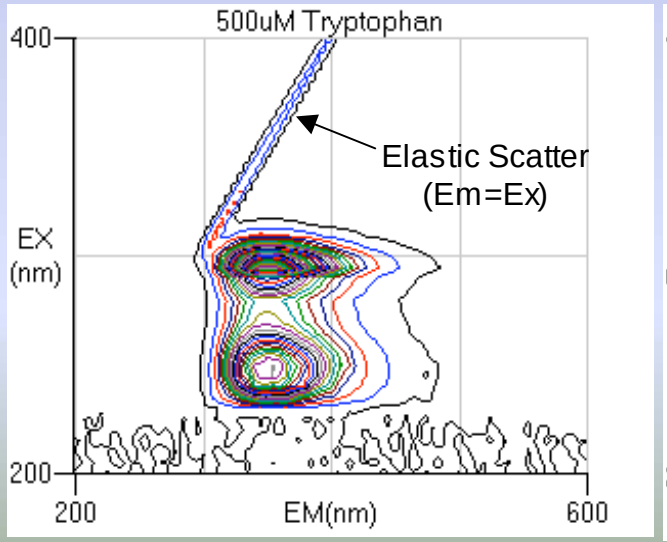
1. Detect and classify organic molecules on rock targets for in situ planetary exploration or terrestrial environmental assessment
2. Detect organic or biological contamination on spacecraft or payload elements
3. Validate cleanliness after institution of planetary protection or forward contamination cleaning measures
4. Map the distribution of water with high spatial resolution on a sediment or rock surface
5. Measure the spatial and temporal distribution of organic chemical pollutants in water

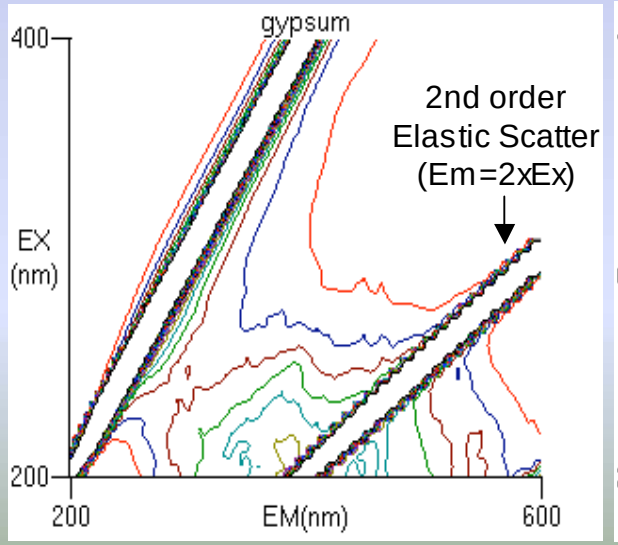
Limits of Detection: parts per trillion for aromatic organic molecules and at a single microbe for organisms.

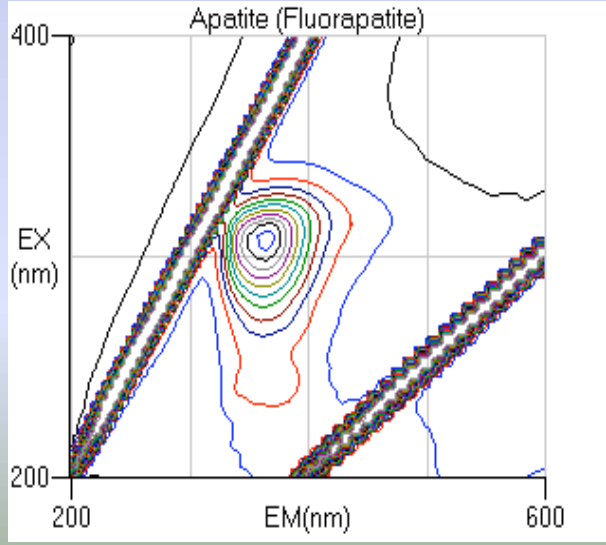
This approach requires no expendables and can operate automatically, remotely by wireless command, or handheld, and it's about the size of a shoebox and can be made smaller.

Advantages of Deep Ultraviolet Excitation LINF

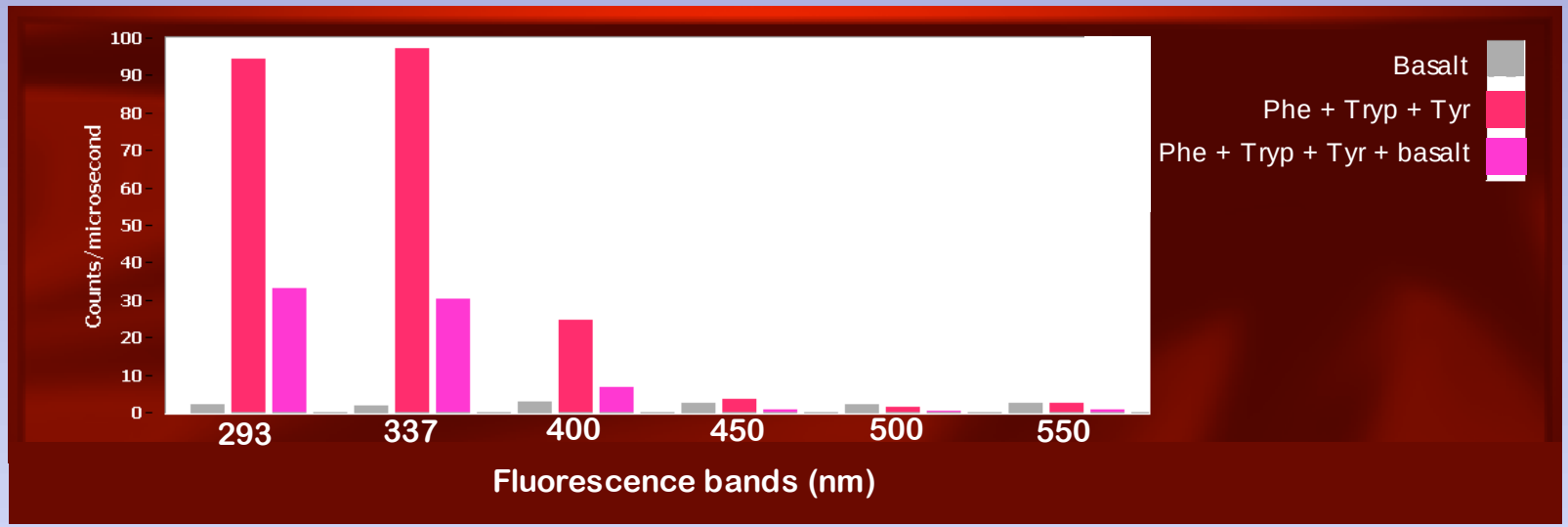
1. The short wavelength is strongly absorbed by conjugated double bonds such as those characteristic of aromatic molecular structures which have a strong fluorescence cross-section.
2. Minerals have a weak fluorescence cross-section and their emissions are typically broad and featureless. Thus it is easy to separate out the emissions of the intended target from background emissions.
3. The narrow line width of the DUV light source we use makes it possible to simultaneously excite a Raman spectrum for the detailed identification of organic molecules, including those that do not fluoresce.
4. Fluorescence is a rapid phenomenon-- the test is fast and ideal for survey and target selection for further study.



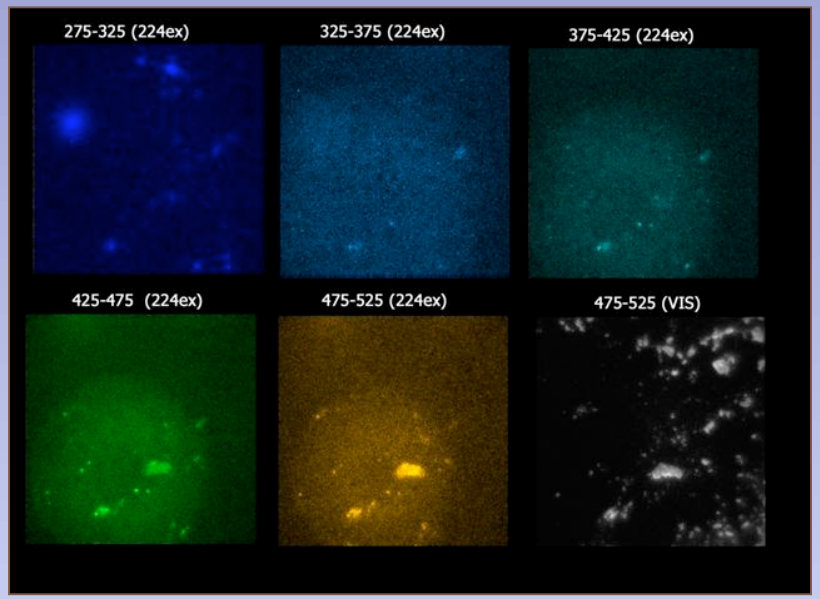


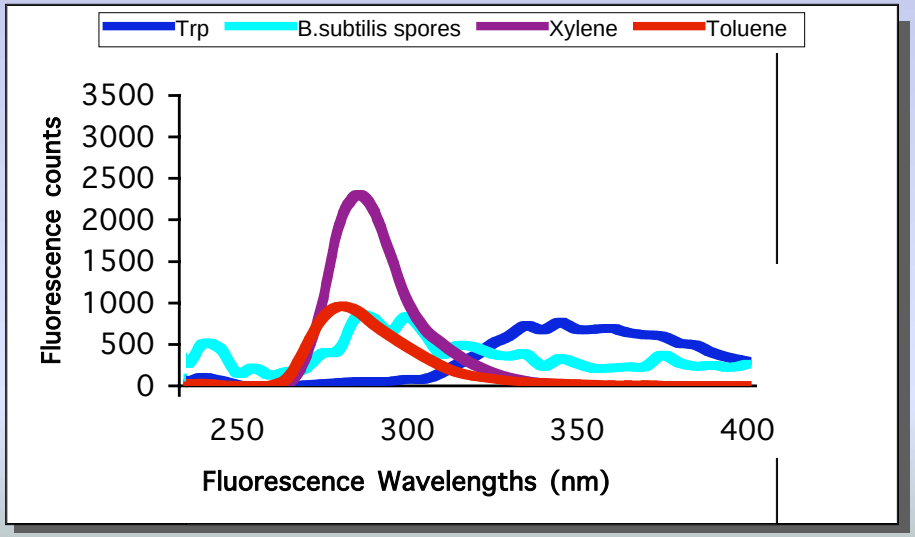


Amino Acid Fluorescence (mixed with basalt)



Laser-induced Native Fluorescence (LINF)





A. 275 - 325 nm
- Single benzene rings
  - tyrosine
  - adenine
  - phenylalanine

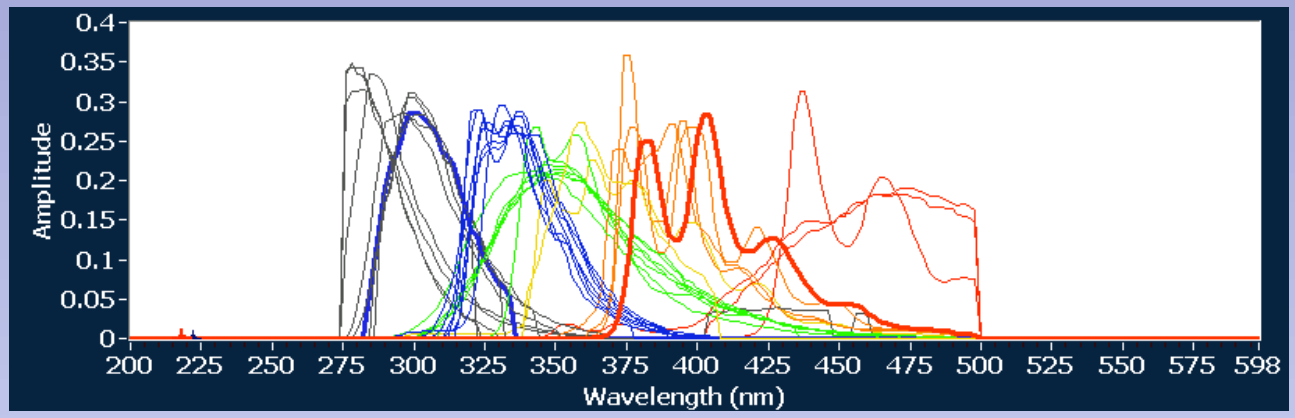
B. 325 - 375 nm
- Tryptophan

C. 375 - 425 nm
- PAHs
- quinones
  in general, molecules with more rings

D. 425 - 475 nm
  riboflavin and NADH

E. 475 - 525 nm
  riboflavin and NADH

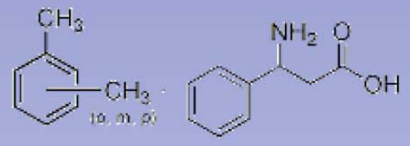
F. Visible reflected light image



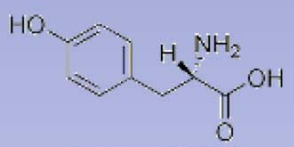
1 Ring	2 Rings	3 Rings	3 Ring (Linear) 4 Ring (Bent)	Indoles	4 Ring (Linear) 5 Rings
xylenes toluene leu-tyr-leu lys-tyr-lys gly-tyr-gly gly-phe-ser gly-phe-ala glu-tyr-glu Dichlorobenzene	1,2 dimethnaphthalene 1,3 dimethnaphthalene 1,4 dimethnaphthalene 1 ethyl naphthalene naphthalene acenaphthene dibenzothioph e n e	1,10 phenanthroline Phenanthrene	anthracene 1 methylanthracene pyrene	carbazole glu-trp-glu leu-trp-leu lys-trp-lys tryptophan	Perylene Fluoranthene

Fluorescence Discrimination Diagram at 235 nm excitation

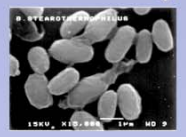
A1: 1 ring with 1-2 methyl groups, and phenylalanine



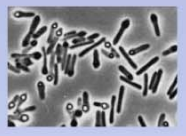
A2: 1 ring with electronegative groups, including tyrosine



B: Bacterial spores

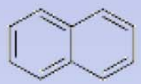


C: Bacterial Cells, Gram +/- and cell lysates

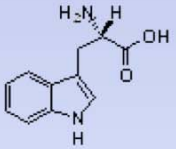


Organisms

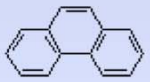
D: 2 rings with or without R groups



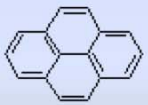
E: Indoles, including tryptophan



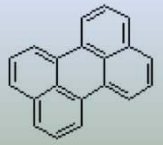
F: 3 rings, bent conformation; ie phenanthrene

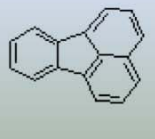


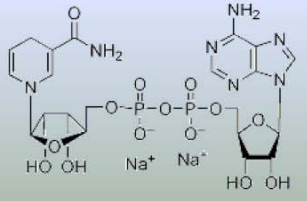
G: 3 rings, straight conformation; or 4 ring folded. ie pyrene

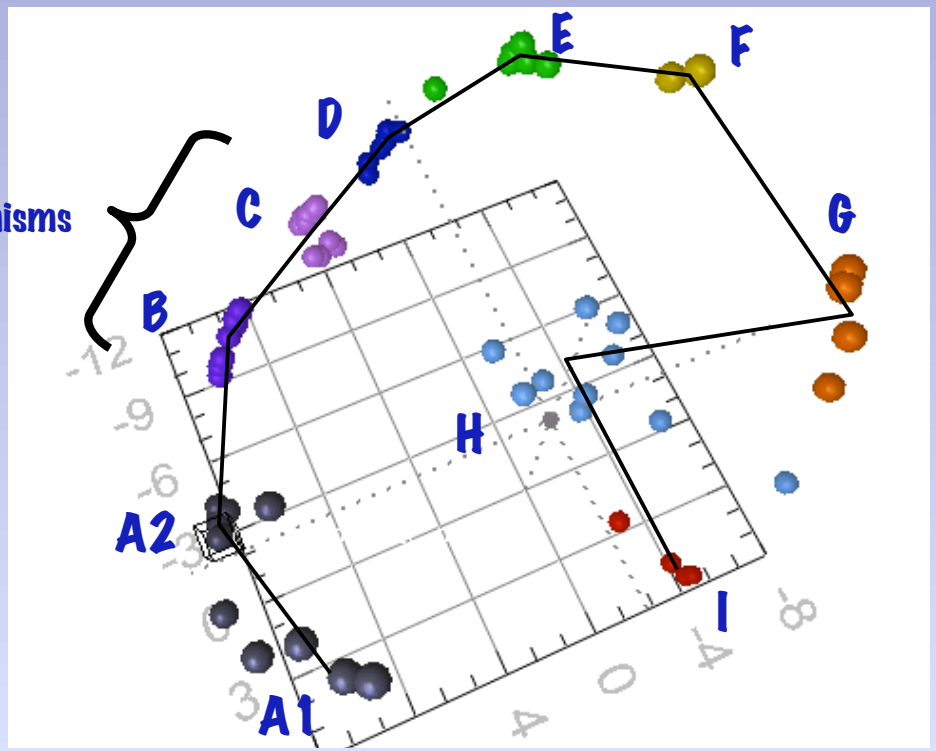


I: 5 rings, folded; and larger ringed organics. ie perylene, NADH etc.

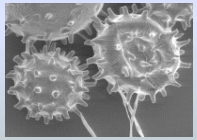






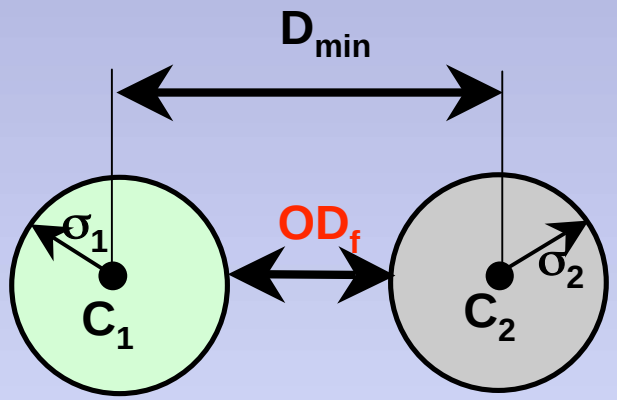


H: Contaminants, ie pollen, drywall, splenda, etc.



Differentiability as a Function of Excitation Wavelength

Overall Differentiability Equation (OD_f)



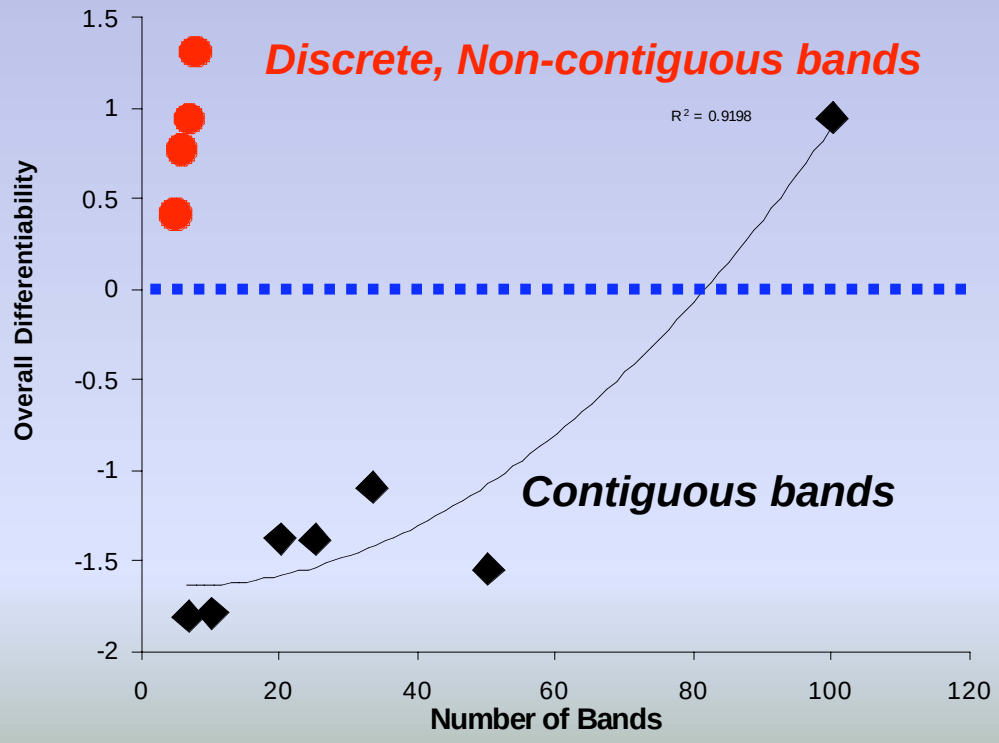
$$OD_f = D_{min} - n(\sigma_1 + \sigma_2)$$

- D_{min} is the distance between the two *closest* clusters whose centroids are C_1 and C_2, within a data set consisting of many clusters.
- σ_1 and σ_2 are the standard deviations for these two clusters
- n is the confidence value correponding to 68.3%, 90%, or 95% (n= 1, 1.645, or 1.960)

Field Instrument

Reduction of Native Fluorescence Spectra to Discrete Bands

- To miniaturize the instrument it is necessary to give up some spectral resolution
- Rather than decreasing the resolution evenly (binning), distinct bands are used to retain molecular specificity

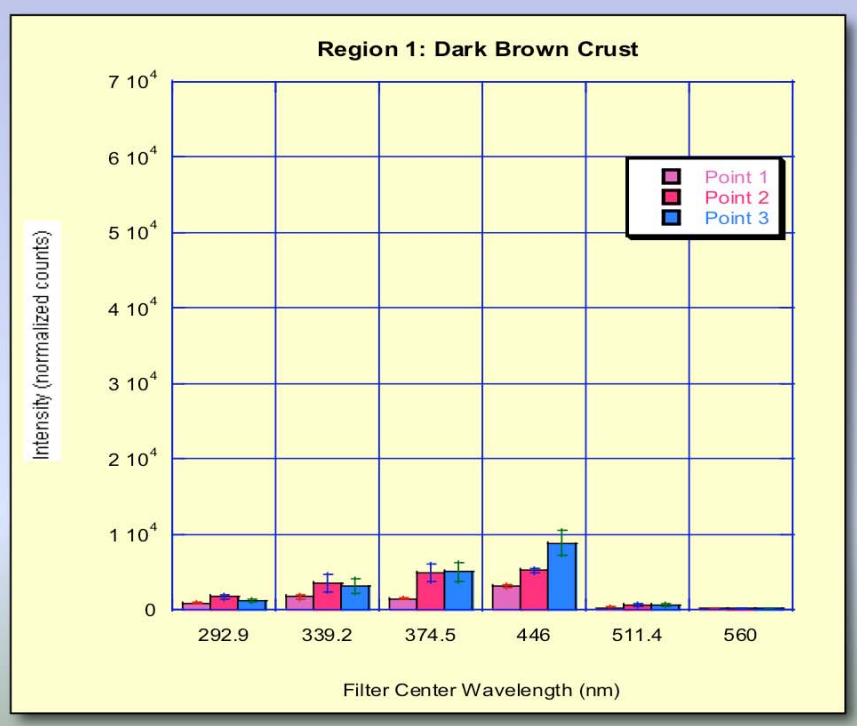


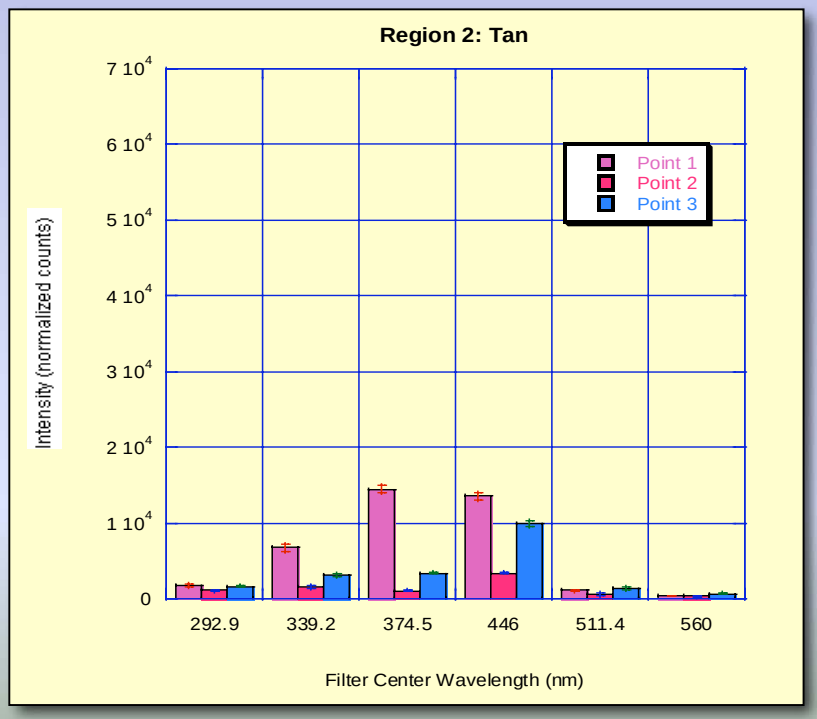
Environmental Assessment

Habitable zones can be considered the way that stratigraphers view marine transgressions and regressions--habitat can surge or retreat and it is heterogeneously distributed.

The heterogeneity and density of this distribution is a measure of whether the ROI is increasing or decreasing in its habitability for the ecosystem present at the moment of observation.

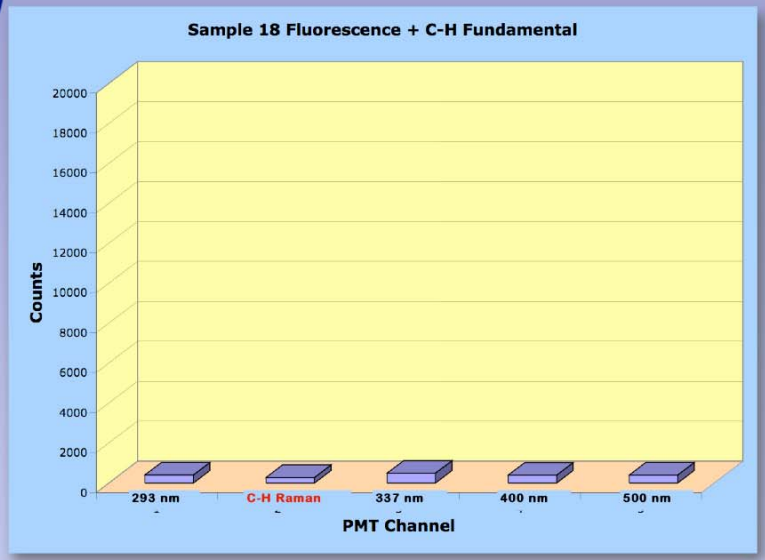
LINF of Antarctic Sandstone Surfaces



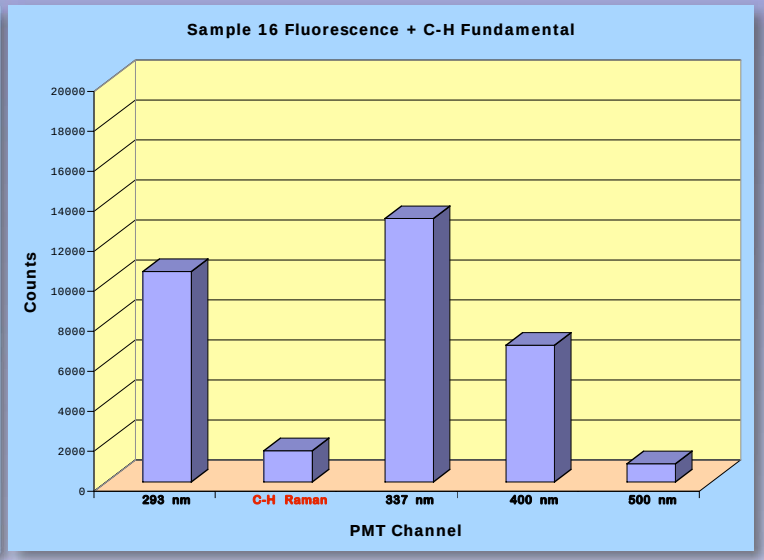


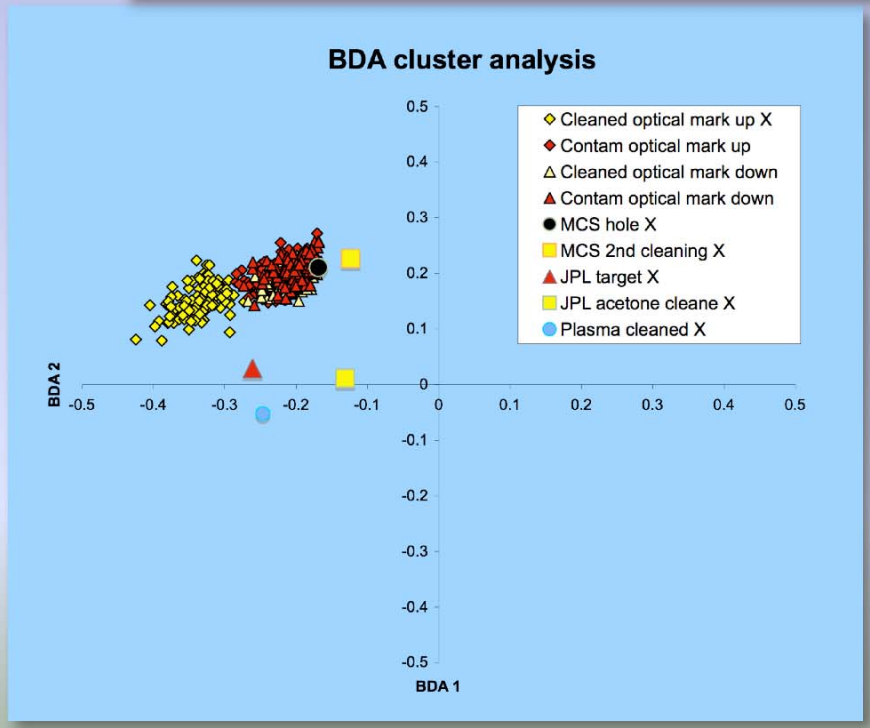
about 1 meter

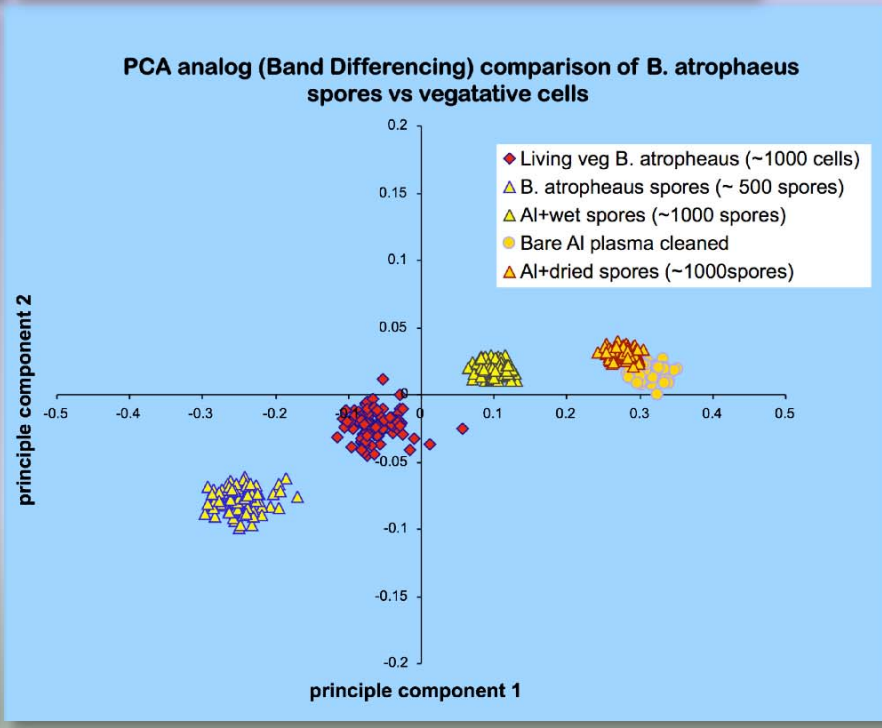
Boulder Interior…



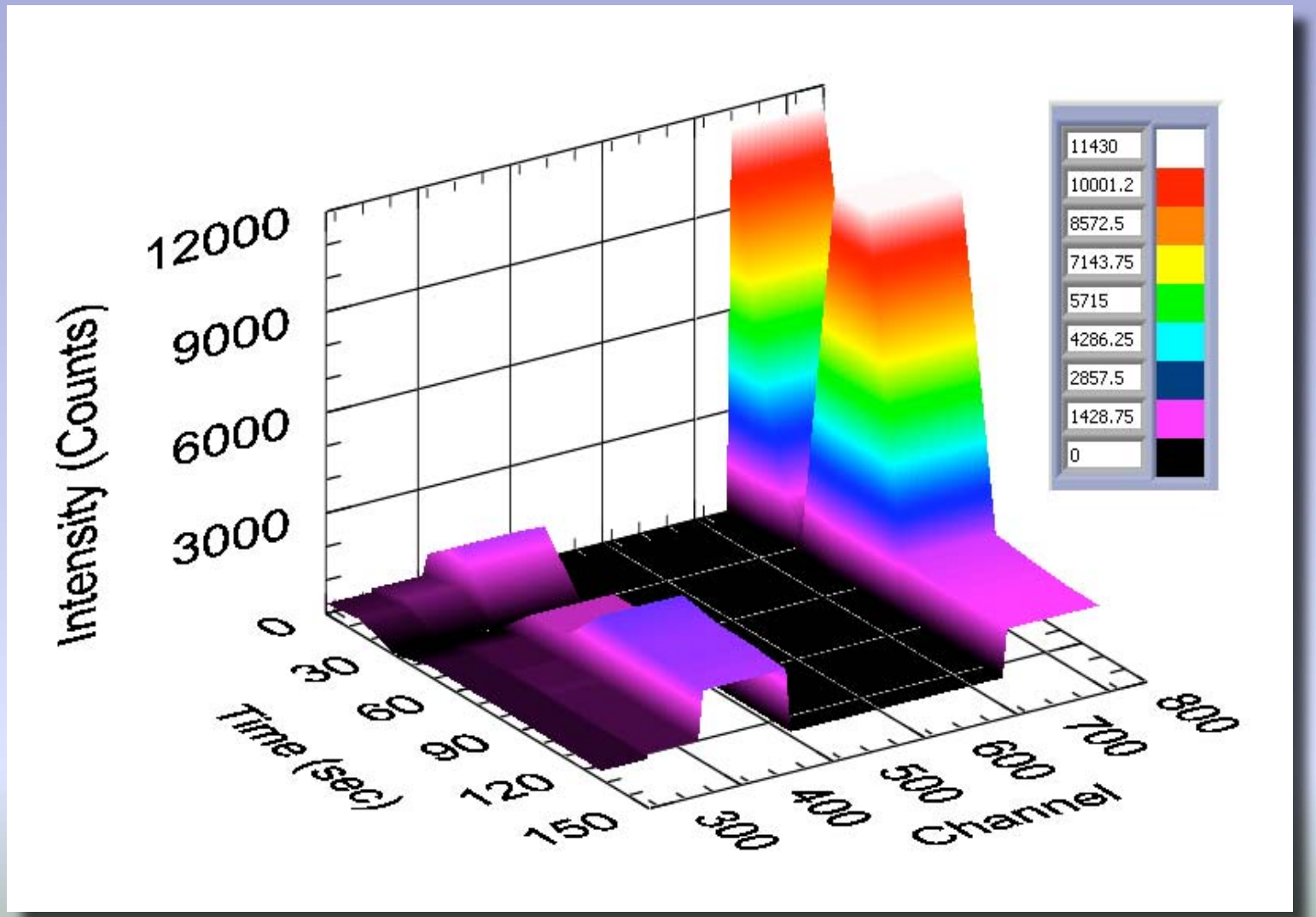
Black lichen LINF on the boulder surface







Passive Luminescence (16 sec) from Black Smoker at Guaymas Basin, Sea of Cortez



This work was funded by the NASA ASTEP program and the JPL Research and Technology Development program.

conrad@jpl.nasa.gov